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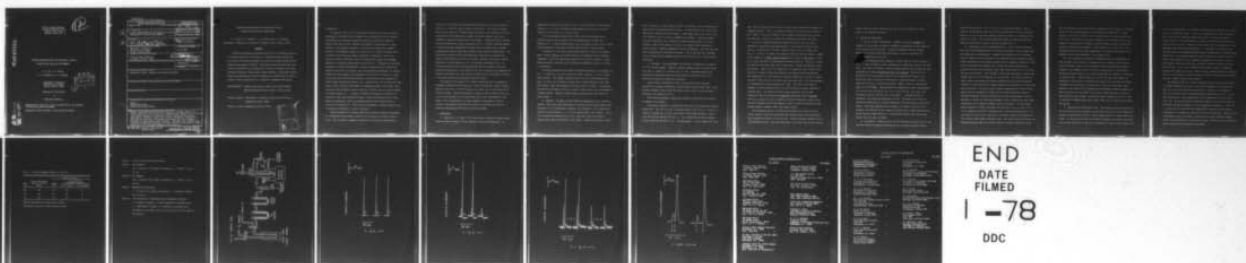
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HYDRIDE PRECONCENTRATION FOR INDUCTIVELY COUPLED
PLASMA OPTICAL EMISSION SPECTROMETRY

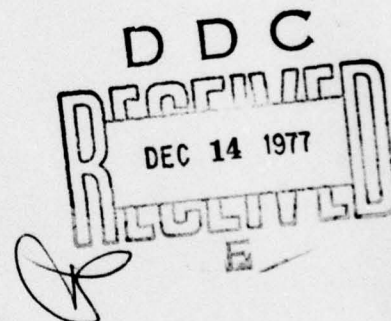
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HYDRIDE PRECONCENTRATION FOR INDUCTIVELY COUPLED
PLASMA OPTICAL EMISSION SPECTROMETRY

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ABSTRACT

Studies are presented describing application of the NaBH_4 reduction of soluble arsenite to form arsine as a preconcentration approach for ultra-trace level arsenic analysis by inductively coupled plasma optical emission spectrometry (ICP-OES). Specialized analyte introduction techniques are described for elimination of reaction by-products that would normally extinguish a medium power plasma discharge. Approaches are presented that eliminate the need for background correction and facilitate superior arsenic sensitivity in a relatively inexpensive ICP system.

INDEX HEADINGS: Emission spectroscopy; Inductively coupled plasma;
Hydride preconcentration; Arsenic; Trace analysis.

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INTRODUCTION

The superior sensitivity of inductively coupled plasma optical emission spectrometry (ICP-OES) to many elements (1) in conjunction with the inherent simultaneous multielemental detection possibilities offered by emission analysis have made the ICP a powerful new method of determination of trace elements in environmental materials. Some toxic non-metals are, however, present in environmental samples at levels too low to detect by either ICP or AA analysis when nebulizer sample introduction is employed. Olson et al. recently reported a detection limit of 10 ppb arsenic using a flow-through approach to ultrasonic nebulization with the ICP (1). Although this technique represents a valuable development in emission spectroscopy and realizes far superior sensitivity (to arsenic) than nebulizer-flame approaches, it, however, remains less than adequate for measurement of the levels of arsenic (< 8 ppb) occurring in many environmental materials such as natural water samples (2). Direct sample introduction methods (e.g., nebulizer) for the ICP have also been shown to lead to severe interference by background spectra (stray light, etc.) resulting from excessively intense emissions of species such as calcium present in complex samples (3). A variety of schemes for background elimination or correction involving interference filters, solar blind photomultiplier tubes, double monochromators, and/or wavelength modulation have been utilized to alleviate the problem (3). A more sensitive approach of reduced susceptibility to spectral interference is clearly desirable.

Hydride generation is commonly employed in atomic absorption spectrometry as a preconcentration method to enhance the sensitivity of arsenic analysis (4,5). This relatively inexpensive alternative to flameless atomization of

arsenic for AA involves near quantitative conversion of the oxidized forms of arsenic in a 25-100 mL sample volume to form arsine. This volatile product flows to the burner as a discrete "plug" of analyte, thus effecting a net pre-concentration that dramatically enhances the atomic spectral sensitivity compared to nebulizer introduction of the sample. Although potential chemical reaction inhibitors are under investigation (6,7), a further advantage appears to include resultant separation of arsenic from the sample matrix, thereby excluding many species that might otherwise cause spectral interferences. The qualities associated with hydride generation techniques are desirable for emission spectroscopy as well as AA and have, therefore, resulted in limited application of this approach to d.c. and microwave discharges (8,9). An inherent problem with the hydride generation that has, however, prevented successful application of this method to the ICP is caused by the quantities of reaction by-products (H_2 , H_2O , and CO_2) produced that can extinguish a medium or low power plasma when introduced along with arsine.

The purpose of this paper is to present separation and low temperature entrapment techniques that exclude the reaction by-products, thereby allowing superior sensitivity in the ICP analysis of arsenic via the generation of its volatile hydride. Resultant separation of analyte from the matrix allows use of a low power plasma (1.2 Kw input power) and a small monochromator (0.35 meter) since the spectrum is no longer complex in the absence of matrix species. Experimental conditions are outlined to eliminate the need for elaborate background processing and correction schemes.

I. EXPERIMENTAL

A. Apparatus. A 27 MHz, 1.2 Kw (input power) inductively coupled plasma torch described elsewhere (10) was employed in these investigations. An

acceptable substitute system would be the 1.5 Kw ICP marketed by Plasma Therm (Kresson, N. J.) or any equivalent system designed for analytical ICP spectrometry at 27 MHz and ≥ 1.2 Kw input power.

A 0.35 meter Heath (Benton Harbor, Mich.) EU-700 monochromator with grating blazed at 250 nm, Heath EU-701-30 photomultiplier module, RCA (Harrison, N. J.) IP28A photomultiplier tube, and Linear (Irvine, Calif.) model 355 potentiometric strip chart recorder were utilized in these studies.

A standard d.c. FET input photo-current amplifier circuit with variable gain, variable damping, and current offset was constructed using a Signetics (Sunnyvale, Calif.) 536 operational amplifier as the basic component. Appropriate grounding, shielding, and filtering were employed to avoid r.f. pickup in the readout.

The hydride generation and sample introduction apparatus are diagrammed in Fig. 1. Symbols V_1 , V_3 , and V_4 represent Teflon stopcocks. V_2 was a ground glass stopcock. The reagent syringe utilized was the standard ground glass type. A 6 mm x 16 mm "football"-shaped Teflon coated stirring bar was used. The reaction vessel was designed to hold up to 25 mL of sample. The capacity can easily be increased to 100 mL by using a larger vessel and an appropriately extended bubbler. NaBH_4 was added through a capillary tip drawn from 2 mm Pyrex tubing.

B. Reagents. 5% NaBH_4 in dilute NaOH was prepared from Alfa Inorganics (Danvers, Mass.) 98% pelletized NaBH_4 or the 99% analytical grade NaBH_4 powder. "Suprapur" (E & M Laboratories, Darmstadt, West Germany) or A.R. Grade hydrochloric acid was diluted to ~ 1 N as the working level in all samples. The As (III) standard was prepared (11) at the 1 ppm level from which 5-200 μL aliquots were taken for addition to the sample. Indicating "Drierite" (Xenia,

Ohio) was used as a drying agent to prevent ice buildup in the cold trap and/or water vapor from extinguishing the plasma. Dry NaOH pellets (A.R. grade) were employed to remove CO_2 from the system. Liquid argon used to cool the 3.17 mm o.d. stainless steel "U" trap is commercially available. Argon may alternatively be liquefied in the laboratory by flowing gaseous argon at 12 L/min through 3 turns (25 mm radius) of 6.35 mm o.d. copper tubing submerged in liquid nitrogen. Multiple submerged coils may be employed. This flow rate and coil configuration is sufficient to produce ~ 400 mL per hour (per submerged coil) of liquid argon streaming from the end of the coil into a second collection dewar.

C. Procedure. The monochromator was directly illuminated at a distance of 13 cm from the plasma. Vertical viewing occurred so that the center of the slit was at a height of 1 cm above the r.f. coil. Horizontal position was optimized by moving the plasma while monitoring a carbon line (247.9 nm) emitted continuously by plasma gas impurities.

Atomic arsenic transitions at 193.7 nm and 228.8 nm were isolated initially by scanning a temporarily mounted arsenic hollow cathode lamp. Final spectral bandpass values chosen for analysis were 0.05-0.1 nm and the photomultiplier was operated at 700 v.

The following procedural steps were evolved for determination of arsenic in natural water samples.

The system is turned on allowing the water bath to equilibrate at approximately 60°C. The 193.7 nm line is isolated using a 25-50 μm slit. Valve V_1 is closed, V_4 opened, and V_2 and V_3 are turned to flow argon through all torch lines for several minutes (see Fig. 1). V_3 is closed and the plasma ignited without "punching the hole" (i.e., "no sample gas"). A 25 mL sample and 2.5 mL

conc. HCl are pipetted into the clean reaction vessel (through the sidearm) and stoppered tightly. Valve V_3 is turned to bypass the plasma with the "sample gas" stream. Valve V_2 is turned to allow eventual reaction products to enter the cold trap. Valve V_4 is closed, the stirring bar activated, and argon (~ 1.5 L/min) is bubbled through the sample for 30 sec. The cold trap is immersed in liquid argon and approximately 15 sec allowed for equilibration. Valve V_1 is turned and 2.5 mL BH_4^- reagent is drawn into the syringe (see Fig. 1). Valve V_1 is turned in the opposite direction and the reagent is added to the sample in a steady dropwise fashion over a period of one minute. Valve V_2 is closed and valve V_4 opened before pressure builds up. Valve V_2 is turned to select the auxiliary argon line ("sample gas"), thereby excluding the reaction vessel. After 5 sec, the "sample gas" is turned off with a needle valve. Valve V_3 is turned to expose the plasma to the eventual cold trap effluent. The "sample gas" is slowly turned on using the needle valve in order to "punch the hole" (final flow rate 0.9 L/min with valve wide open). The chart recorder is activated (full scale equivalent 10^{-8} amp). The liquid argon dewar is removed, 3 sec are allowed to pass, and the cold trap is quickly immersed in lukewarm water. The transient arsenic signal appears at the recorder completely time resolved from any significant background signal variation. Valve V_3 is closed, the cell is emptied and rinsed through the sidearm using the probe attached to the water aspirator, and all steps are repeated for subsequent samples, standard "adds," and reagent blanks.

This procedure results in conversion of arsenate and arsenite (12) to arsine, removal of H_2O and evolved CO_2 from the gas stream, and preconcentration entrapment of arsine in the cold trap. Evolved H_2 passes through the cold trap bypassing the ICP. When the temperature of the cold trap is later raised,

arsine enters the plasma (free from H_2O , H_2 , and CO_2), degrades to atomic species, and undergoes excitation.

II. RESULTS AND DISCUSSION

A. Direct Product Introduction. Running the reaction without cold trapping or drying agent resulted in immediate extinguishing of the plasma due to the quantities of H_2 evolved. Procedures frequently used for hydride generation for atomic absorption spectrometry (4,5) are, therefore, not directly appropriate for the ICP.

B. Cold Trapping and CO_2 Hindrance. Liquid argon was used as coolant in place of liquid nitrogen to avoid condensing the "sample gas" argon in the cold trap. The plasma was, however, further extinguished when drying agent and cold entrapment were used if pelletized reagent was employed. Observation of a pronounced 516.5 nm C_2 emission high in the "recombination" region of the plasma just prior to extinction confirmed the suspected presence of large quantities of CO_2 as a reaction by-product. $MgCO_3$ is used as a pelletizing agent in the 98% $NaBH_4$. When acidified and degassed with argon, large amounts of CO_2 evolve and build up as "dry ice" in the cold trap. This CO_2 is not tolerated as well by the ICP as it is by flames. It emerges rapidly to extinguish the plasma upon warming of the trap. Subsequent use of 99% non-pelletized reagent and a 1.5 L/min "sample gas" flow rate greatly reduced the effect. The plasma remained intact; however, an intense C_2 emission still occurred, the character of the plasma was altered, and a large transient background recorder signal (see Fig. 2) obscured any response from 100 ng added arsenic when the trap was warmed.

C. CO_2 Removal. Addition of the tube of NaOH pellets shown in Fig. 1 was the final factor in removing remaining CO_2 and allowing successful arsenic

detection using the 193.7 nm line and a 0.2 nm spectral bandpass. The C_2 emission (recombination region) was totally suppressed for the 98% pelletized $NaBH_4$ as well as for the more expensive analytical grade at a sample gas flow rate of 0.9 L/min. The transient background signal was greatly reduced and superior sensitivity to arsenic (100 ng) resulted (Fig. 3).

D. Improvement of Line-to-Background Ratio. Figs. 2 and 3 illustrated that the line-to-background ratio was far more important in these studies than any signal/noise considerations. Expanded scale detection of 10 ng arsenic (Fig. 4) manifests the persistence of two remaining smaller background signals. Visual observation of the plasma confirmed that the momentary reduction in size of the traditional ICP "doughnut hole" raises the plasma background and accounts for the initial transient signal upon sudden removal of the cold trap from the coolant dewar. This transient is much more pronounced if larger trap volumes than the 3.17 mm stainless "U" are utilized. Monitoring of the 193.1 atomic carbon line during trap warming confirmed that the second background transient is most likely due to organic species that condensed in the cold trap during collection. The stray light increase accompanying the intense atomic carbon emission undoubtedly accounts for the second background transient. Although background correction schemes and/or larger spectrometers could be employed to correct the remaining background, Table I demonstrates that simple exploitation of the spectral bandpass solves the problem. The second background transient is barely detectable (4X less than in Fig. 4) when a 25 μ m slit is employed, and Table I indicates that it may be neglected since it is less than 1% of the line at the level (~ 100 ng As) normally encountered in a 25 mL natural water sample (baseline level). For lower levels than 100 ng, the background appears small and constant enough to measure separately in time

(non-automatically) and subtract from all subsequent sample signals. Continued use of the small monochromator in non-background corrected mode is thereby allowed. The 228.8 nm line may also be used where no close-lying carbon emissions occur. The initial spike due to changes in the "doughnut hole" is also reduced at smaller spectral bandpass values even when the gain is increased to maintain constant arsenic response. These effects are a result of the well-recognized nonlinear (2nd power) dependence of continuous-like spectra on the bandpass versus linear dependence of line spectra (13).

The carbon background transient is rendered virtually insignificant at small bandpass values and Fig. 5 demonstrates that complete time resolution (from the arsenic signal) of the remaining initial background spike (due to changes in the "doughnut hole") is readily accomplished if a short delay is introduced between removal of the liquid argon dewar and immersion of the trap in lukewarm water. Delay periods up to 10 sec have been tried without any emergence of arsine prior to immersing the trap in the water bath and without subsequent loss in precision or sensitivity. When the liquid argon trap is removed, a thin sheet of ice (condensate from atmospheric humidity) appears to form immediately on the exterior of the trap, thereby helping to insulate it from excessive rapid warming. Arsine then remains trapped until the "U" tube is immersed in lukewarm water which rapidly melts the ice film and volatilizes the analyte.

E. Sensitivity and Detection Limits. The detection limit was measured to be 0.5 ng arsenic which represents 20 parts-per-trillion in a 25 mL sample and would be 5 parts-per-trillion on a 100 mL sample basis (if a larger vessel were used). It should be noted that this report of dramatic (500-2000X) improvement over earlier reports of 10 ppb (2) is conservative in that it was achieved with

very little optimization. For example, no optimization of gas flow or vertical position was made for arsenic. A very poor responding (RCA 1P28) photomultiplier tube for this wavelength region (193.7 nm) was operated at moderate voltage (700 v). The spectrometer was directly illuminated at an unfavorably large distance of 13 cm. Narrow slit values (25-50 μm) were employed in a non-background corrected small monochromator. A "home-made," low power ICP was used and simple, non-integrated analog readout was employed on a transient peak height basis. The resultant superior arsenic sensitivity was seen to occur in spite of the absence of further parameter optimization as soon as the basic difficulties involving H_2 , H_2O , CO_2 , and argon condensate (in the cold trap) were overcome. Figs. 3 and 4 demonstrate that arsenic levels (1-8 ppb) in natural water samples are easily within the newly expanded sensitivity range of the ICP. The response is linear to weight of arsenic added and also to concentration if sample volume is held constant.

The detection limit on an analog (signal/2x noise) basis was not found to be strongly dependent (see Table I) on spectral bandpass or on whether the 193.7 nm or 228.8 nm transition was employed. Choice of 0.2 nm bandpass (100 μm slit) and/or λ 228.8 nm produced signal enhancements of four- and ten-fold, respectively, when compared with 0.05 nm bandpass (25 μm slit) and/or λ 193.7 nm. The limiting noise contribution, however, was due to variation of the plasma emission background. It also increased accordingly by ~ four- and ~ ten-fold at 100 μm and 228.8 nm, respectively, producing no net dramatic improvement in the signal-to-noise ratio or limit of detection. Since the line-to-background ratio was, however, improved at the lesser spectral bandpass, 25-50 μm was maintained as the chosen slit range. Either 193.7 nm or 228.8 nm may be employed as the analytical wavelength.

Samples much smaller than 25 mL may be analyzed by pipetting the sample (or micro-sample) into a 25 mL volume of 1 N HCl. Resultant concentration sensitivity will decrease accordingly, but the 0.5 ng absolute weight detection limits will remain easily achievable making the procedure applicable to a wide variety of clinical and environmental samples of very low arsenic content.

III. CONCLUSIONS

Hydride preconcentration has proved to be a relatively inexpensive, viable approach to sensitivity enhancement for arsenic analysis with the ICP when the effects of H_2 , H_2O , CO_2 , and argon condensate are controlled.

The method of CO_2 elimination employed in these studies would preclude exploitation of H_2Se , H_2Te , and H_2Po (owing to their small pKa values relative to AsH_3) in a preconcentration approach. Although further species were not investigated, Ge, Sn, Sb, Bi (as hydrides), and possibly Hg (as Hg^0) should, however, remain under consideration as candidates for preconcentration ICP approaches similar to that employed in these investigations for arsenic. If multichannel detection facilities are available, these elements could then be preconcentrated and detected simultaneously in the ICP as cannot be done using conventional AA approaches. Less expensive separation schemes such as those reported for atomic absorption (14) could also be coupled with the techniques described herein to distinguish the form (inorganic versus "alkyl-substituted") of a given group IV or V element present in the sample by ICP spectrometry.

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Table I. Spectral Bandpass Effects at 193.7 nm.

Slit (μm)	Line-to-Background Ratio at 100 ng Level	Weight (ng)	Detection Limits	
			Concentration (parts-per-trillion)	
			25 mL Sample ^a	100 mL Sample ^b
100	28.	0.5	21.	5.
50	56.	0.6	23.	6.
25	112.	0.7	29.	7.

^aValues realized in existing reaction vessel.

^bProjected values for a larger reaction vessel.

Figure 1. Hydride Preconcentration Apparatus.

Figure 2. CO₂ Hindrance.

a,b. = 100 ng As (III) added in duplicate; c. = "blank"; slit is 100 μ m.

Figure 3. CO₂ Removed.

a,b. = 100 ng As (III) added in duplicate; c. = "blank"; slit is 100 μ m.

Figure 4. Expanded Scale Detection.

a. = 10 ng As (III) added in duplicate; b. = duplicate "blanks"; slit is 50 μ m..

Figure 5. Time Resolution of Remaining Initial Background Transient.

a. = removal of dewar; b. = rapid immersion in lukewarm water;
c. = 2nd removal of dewar; d. = immersion in lukewarm water
following a 3 sec delay; slit is 100 μ m; 100 ng As (III) added to
both trials.

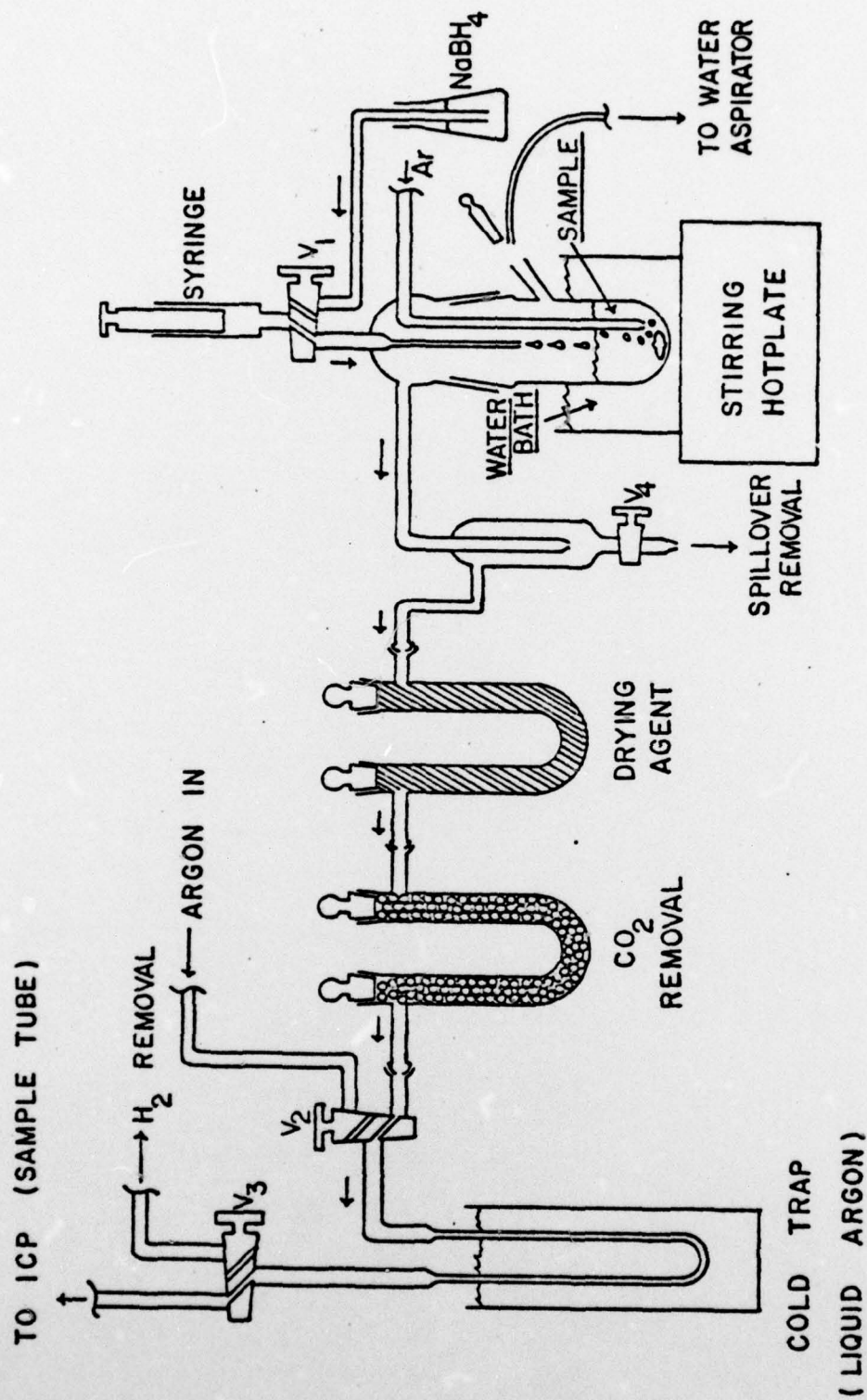


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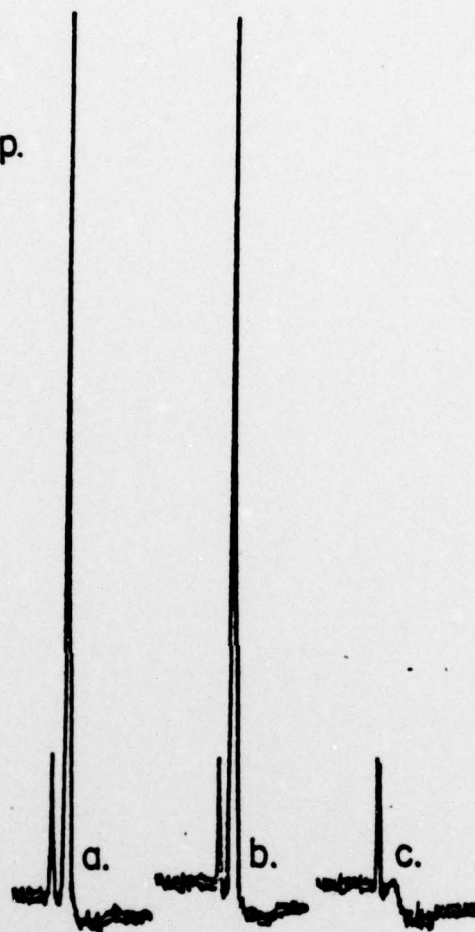


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10^{-9} amp.

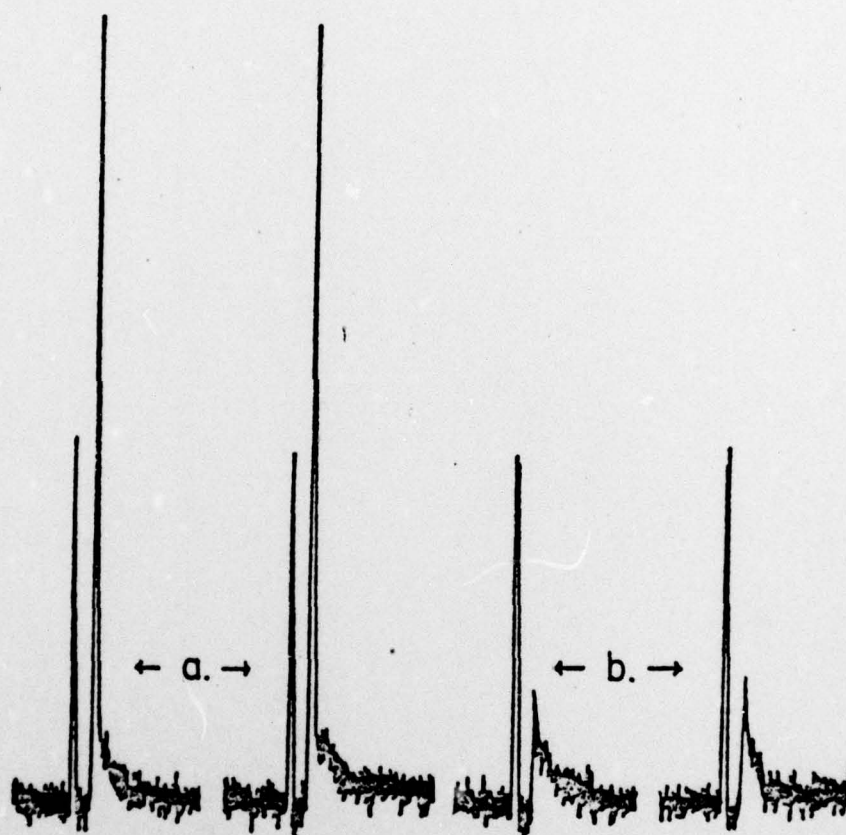


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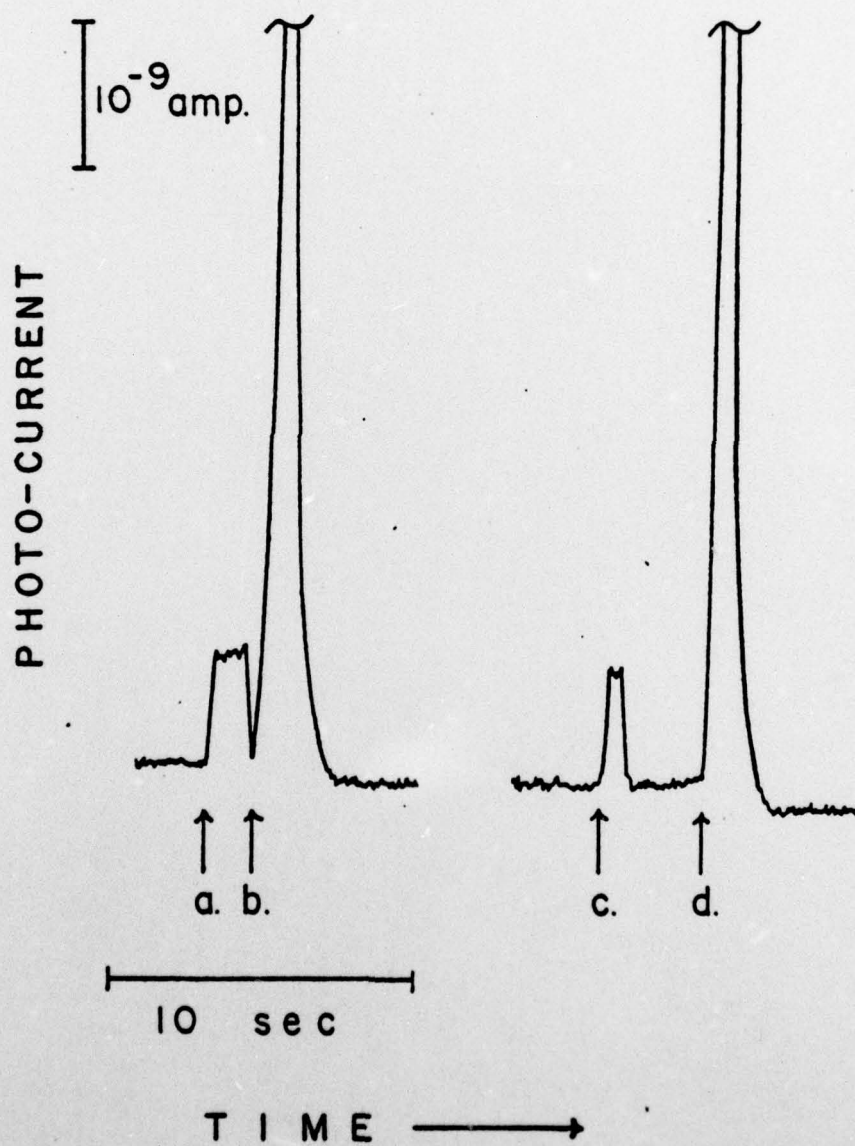
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